



Europäisches Patentamt

(19)

European Patent Office

Office européen des brevets

(11) Publication number:

0 073 087

A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82201044.3

(51) Int. Cl.³: **C 08 F 234/02**

(22) Date of filing: 19.08.82

//(C08F234/02, 214/26, 210/00,
214/18)

(30) Priority: 20.08.81 US 294789

(71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY
Legal Department 1007 Market Street
Wilmington Delaware 19898(US)

(43) Date of publication of application:
02.03.83 Bulletin 83/9

(72) Inventor: Squire, Edward Noonan
P.O. Box 120 R.D. 2
Glen Mills Pennsylvania 19342(US)

(64) Designated Contracting States:
DE FR GB IT NL

(74) Representative: van der Beek, George Frans et al,
Nederlandsch Octrooibureau Johan de Wittlaan 15 P.O.
Box 29720
NL-2502 LS Den Haag(NL)

(54) Amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole.

(57) Amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene and, optionally, with another ethylenically unsaturated monomer, have high glass transition temperatures, e.g., 85°C or higher, low indices of refraction, and good physical properties which make them suitable for high-temperature, high-transparency applications.

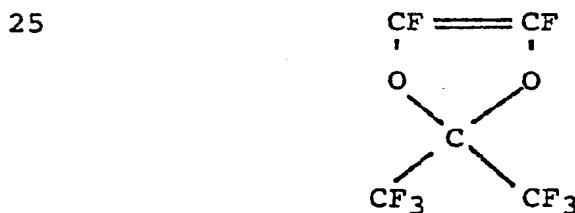
EP 0 073 087 A1

TITLEAmorphous Copolymers of Perfluoro-2,2-di-
methyl-1,3-dioxoleBACKGROUND OF THE INVENTION

5 This invention relates to certain amorphous perfluoropolymers which are particularly suitable in high-temperature applications requiring high clarity and transparency.

10 Fluoropolymers have found wide use in applications requiring good performance under a variety of temperature and atmospheric conditions and resistance to many chemicals. Where clarity and transparency are important considerations, polymers should be completely amorphous because crystallites 15 present cause light scattering. For high-temperature applications, a polymer should have a high glass transition temperature, T_g , because above its T_g it would lose some of its desirable physical properties. Entirely amorphous fluoropolymers having 20 significantly high T_g 's have not been heretofore reported.

U.S. Patent 3,978,030 to Resnick describes certain polymers of perfluoro-2,2-dimethyl-1,3-dioxole (PDD), which has the following formula:



30 The above patent describes both homopolymers of PDD, which are not further characterized, and a crystalline copolymer with tetrafluoroethylene (TFE), which has a melting point of about 265°C.

SUMMARY OF THE INVENTION

According to this invention, there is now provided a class of amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole with

5 tetrafluoroethylene and, optionally, with at least one other ethylenically unsaturated monomer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of the molar fraction of PDD in the dipolymer versus the Tg of the dipolymer.

10 FIG. 2 is a graph representing two wide-angle X-ray powder diffraction scans, respectively, of an amorphous PDD/tetrafluoroethylene copolymer of the present invention and of a prior art crystalline copolymer.

15 DETAILED DESCRIPTION OF THE INVENTION

Both principal monomers used in this invention are known to the art. TFE is made in large quantities by E. I. du Pont de Nemours and Company, while PDD is described in the above-mentioned U.S.

20 Patent 3,978,030. Pure PDD boils at about 33°C at atmospheric pressure. It has now been discovered that these two monomers can be copolymerized in all weight proportions within the range of 1-99 percent TFE.

25 This discovery is very surprising because no other perfluoro monomer is known to copolymerize with TFE in all proportions except perfluoro-2-methylene-4-methyl-1,3-dioxolane, which is a completely different type of monomer that has an

30 exo-perfluoromethylene group. PDD, on the other hand, has an endo-double bond. In fact, other perfluoro monomers having internal double bonds copolymerize with TFE with extreme difficulty. Monomers such as perfluoropropyl vinyl ether and

35 hexafluoropropylene copolymerize with TFE with such

difficulty that copolymers with TFE containing more than 20 mole % of such monomers are not commercially feasible.

As the amount of PDD in the copolymer

5 increases, the Tg also increases, although not necessarily in a linear fashion. The relationship between the molar fraction of PDD in the dipolymer and the Tg is shown in FIG. 1. It can be seen that a copolymer containing 11.2 mole percent PDD has a Tg

10 of 57°C, and a copolymer containing 56.9 mole percent PDD has a Tg of 119°C. Copolymers having intermediate amounts of PDD also have intermediate Tg's. Tg is determined by differential scanning calorimetry (DSC) according to ASTM method D-3418.

15 It has been found that copolymers of PDD and TFE in which the amount of PDD is less than about 11 mole percent are normally crystalline. Although the exact breakpoint for crystalline character has not been established with certainty, it is believed that

20 copolymers having 7 mole percent or less of PDD are all crystalline. The relative proportions of the comonomers in the copolymer can be determined by fluorine-19 nuclear magnetic resonance spectroscopy (NMR). The proportion of hydrogen-containing

25 monomers can be determined by proton NMR together with ¹⁹F NMR. The relative proportions and reactivities of the various monomers in a copolymer correspond more or less to the proportions of the starting monomers in the polymerization reaction.

30 A homopolymer of PDD appears to be amorphous and has a high Tg. However, PDD is a much more expensive monomer than TFE so that use of PDD homopolymers, rather than of PDD/TFE copolymers, is economically much less attractive. Furthermore, the

35 copolymers are easier to fabricate. The dipolymers

have low refractive indices, and films of these copolymers are clear and transparent, compared with hazy or translucent films of crystalline polymers. For this reason, the amorphous copolymers of the 5 present invention are suitable for such applications as, for example, windows for chemical reactors, especially for processes using or manufacturing hydrogen fluoride. Amorphous terpolymers can be made by copolymerizing certain ethylenically unsaturated 10 monomers with perfluoro-2,2-dimethyl-1,3-dioxole and tetrafluoroethylene. These include selected olefins, vinyl compounds, and perfluoromonomers. Typical olefins are, for example, ethylene, propylene, 1-butene, isobutylene, trifluoropropene, and 15 trifluoroethylene. Vinyl monomers can be, for example, vinyl fluoride, vinylidene fluoride, and chlorotrifluoroethylene. Perfluoromonomers may be of different chemical types, for example, perfluoropropene, perfluoro(1,3-dioxole), 20 perfluoro(alkyl vinyl ethers), methyl 3-[1-[difluoro-[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoropropanoate $\text{CF}_2=\text{CFOCF}_2\text{CFOCF}_2\text{CF}_2\text{COOCH}_3$, and CF_3 25 2-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoroethanesulfonyl fluoride $\text{CF}_2=\text{CFOCF}_2\text{CFOCF}_2\text{CF}_2\text{SO}_2\text{F}$. CF_3

The proportion of PDD in the amorphous 30 terpolymers of this invention should preferably be at least 12 mole percent of the TFE content, while the mole percent content of the third monomer should be the smallest of all three monomers. Outside these limits either an amorphous terpolymer may not be

obtained or, if made, its maximum tensile modulus and strength may not be realized.

Copolymerization is carried out in the presence of a free radical generator, preferably at a 5 slightly elevated temperature, for example, 55-65°C. Well agitated pressure equipment should be used.

This invention is now illustrated by the following examples of certain preferred embodiments thereof, where all parts, proportions, and 10 percentages are by weight, unless otherwise indicated. All Tg's were determined using Du Pont Differential Thermal Analyzer Models 900 or 990. All units other than SI have been converted to SI units.

EXAMPLE 1

15 A 110 cm³ stainless steel shaker tube was charged with a cold solution of 8.2 g (0.0336 mole) PDD and 0.006 g of perfluoropropionyl peroxide in 120 g of 1,1,2-trichloro-1,2,2-trifluoroethane. The tube was closed and chilled further to about -50°C, then 20 alternately evacuated and quickly flushed with nitrogen three times. The cold, evacuated tube was mounted in a horizontal shaker and charged with 2 g (0.02 mole) of TFE. The tube was agitated and heated at autogenous pressure to 50-55°C and maintained in 25 this temperature range for two hours. After cooling and venting the tube, the liquid contents were removed; 1,1,2-trichloro-1,2,2-trifluoroethane was distilled off, and the remaining solid polymer was dried in a vacuum oven at 110°C for sixteen hours. 30 The Tg of the copolymer was 119°C. The apparent melt viscosity (AMV) was 0.9 kPa.s at 230°C. This value was calculated from the melt flow rate (MFR) determined according to ASTM D2116 at a load of 383.1 g at 230°C.

$$AMV \text{ (Pa.s)} = \frac{6.4 \times \text{load (g)}}{\text{MFR (g/10 min)}}$$

NMR analysis of the copolymer showed that it contained 56.9 mole percent PDD and 43.1 mole percent TFE.

5

EXAMPLE 2

Following the procedure of Example 1, a 400 cm³ stainless steel shaker tube was charged with 270 g of 1,1,2-trichloro-1,2,2-trifluoroethane, 30 g (0.123 mole) of PDD, 0.08 g of bis(4-t-butylcyclohexyl) peroxydicarbonate, and 40 g (0.4 mole) of TFE. The tube was agitated five hours at 55-65°C. The resulting copolymer, 49.6 g, was isolated as described in Example 1. Its Tg was 73°C.

15

EXAMPLE 3

Following the procedure of Example 2, a 110 cm³ tube was charged with 120 g of 1,1,2-trichloro-1,2,2-trifluoroethane, 9 g (0.0369 mole) PDD, 0.03 g of bis(4-t-butylcyclohexyl) peroxydicarbonate, and 4 g (0.04 mole) of TFE. Heating 4 hours with agitation at 60°C produced 10 g of copolymer which had Tg's at 102 and 104°C. Extracted overnight with the polymerization solvent, the product gave three fractions. The least soluble fraction (about 70 percent of the total) had a Tg of 105°C and an apparent melt viscosity of 1.65 kPa.s. NMR analysis showed that it contained 43.7 mole percent PDD and 56.3 mole percent TFE. The more soluble fractions had Tg's, respectively, at 99° and 101°C.

30

EXAMPLE 4

Following the procedure of Example 1, a 110 cm³ shaker tube was charged with 100 g of 1,1,2-trichloro-1,2,2-trifluoroethane, 9.8 g (0.0402 mole) of PDD, 6 g (0.06 mole) of TFE and 0.03 g of

35

bis(4-*t*-butylcyclohexyl) peroxydicarbonate. The agitated tube was heated five hours at 53-63°C under autogenous pressure. The resulting copolymer weighed 9.1 g. It was found by DSC to have physical 5 transitions at 74°C, 82°C, 122°C and 124°C. Soxhlet extraction of the copolymer with 1,1,2-trichloro-1,2,2-trifluoroethane gave three polymeric fractions: the least soluble, $T_g = 92^\circ\text{C}$; the middle solubility fraction, $T_g = 93^\circ\text{C}$; and the 10 most soluble, $T_g = 70^\circ\text{C}$.

EXAMPLE 5

Following the general procedure of Example 2, copolymerization of 5 g (0.0205 mole) of PDD, 10 g (0.1 mole) of TFE, and 2 g (0.0714 mole) of ethylene 15 gave 11.3 g of an amorphous terpolymer, which had glass transitions at 70°C, 72°C, 144°C and 151°C.

When this experiment was repeated using only 1 g of ethylene, 12.7 g of an amorphous terpolymer was obtained, which had glass transitions at 63°C and 20 143°C. A film was pressed from this terpolymer at 230°C. Its infrared spectrum was consistent with that of a terpolymer of TFE, PDD, and ethylene. After extraction to remove any trace of shaker tube lubricant, the film had glass transitions at 67°C and 25 71°C.

EXAMPLE 6

Following the general procedure of Example 2, copolymerization of 5 g (0.0205 mole) of PDD, 10 g (0.1 mole) of TFE, and 0.5 g (0.00893 mole) of 30 isobutylene gave after 3 hours at 55-80°C 3 g of a terpolymer, which had glass transitions at 68°C and 76°C. A film pressed from this polymeric material gave an infrared spectrum consistent with that of a PDD/TFE/isobutylene terpolymer.

EXAMPLE 7

A terpolymer of PDD, TFE, and propylene was obtained under the general conditions of Example 2 from 4 g (0.0164 mole) of PDD, 10 g (0.1 mole) of TFE, and 1 g (0.0238 mole) of propylene. The terpolymer weighed 0.7 g, was elastomeric and readily soluble in the polymerization solvent. A film cast from that solvent had infrared absorbancies which confirmed the terpolymer composition.

10

EXAMPLE 8

A terpolymer was prepared according to the general procedure of Example 2 from 4 g (0.0164 mole) of PDD, 10 g (0.1 mole) of TFE, and 1 g (0.00213 mole) of 2-[1-[difluoro[(trifluoroethenyl)-oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoroethanesulfonyl fluoride. This terpolymer weighed 10.8 g and was shown by NMR analysis to consist of 87.1 mole percent TFE, 12.3 mole percent PDD, and 0.6 mole percent of the sulfonyl fluoride monomer. Its infrared spectrum also was consistent with this composition. The terpolymer had glass transitions at 67°C, 124°C, 152°C and 175°C.

EXAMPLE 9

A terpolymer was made according to the general procedure of Example 2 from 3 g (0.0123 mole) of PDD, 10 g (0.1 mole) of TFE, and 1 g (0.00237 mole) of methyl 3-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoropropanoate. The terpolymer weighed 10.2 g. It was pressed at 250°C into a film, which had infrared absorbancies consistent with the terpolymer composition. Fluorine-19 NMR analysis gave the respective mole percent amounts of the three monomers as 83.7 TFE, 13.4 PDD, and 2.9 methyl ester monomer. Differential thermal analysis of the

terpolymer between 25 and 350°C showed the absence of a melting point.

EXAMPLE 10

A copolymer of PDD and TFE was made
5 according to the general procedure of Example 1 from 8 g of PDD and 0.5 g of TFE. This copolymer had the expected infrared absorption and showed glass transitions at 167°C, 215°C and 288°C.

COMPARATIVE EXAMPLE

10 A copolymer was made from 2 parts of PDD and 10 parts of TFE according to the exact procedure of Example 3 of U.S. Patent 3,978,030 to Resnick. This polymeric product was extracted for 25 hours with 1,1,2-trichloro-1,2,2-trifluoroethane. About 0.2
15 percent of the product weight was thus removed; the extracted fraction was a grease and appeared to consist of shaker tube lubricant and a small amount of an unknown fluorocarbon. Because this obviously was a low molecular weight material, it was expected
20 that the material would have a Tg well below 200°C, if it had a Tg at all. The extracted product had no Tg between 25 and 200°C. It was different from the amorphous copolymers of this invention. The solid extraction residue was a crystalline, rather than an
25 amorphous polymer. This comparative experiment shows that at monomer ratios employed in Example 3 of U.S. Patent 3,978,030 no amorphous PDD/TFE copolymer is obtained.

FIG. 2 shows wide-angle X-ray powder
30 diffraction scans of the solid extraction residue of the crystalline polymeric product of this example (curve A) and of an amorphous TFE/PDD copolymer having a Tg of 73°C (curve B). In this figure, intensity, I (counts/sec) is plotted against the
35 diffraction angle, 2θ. The presence of crystallinity

is shown by the sharp peak in curve A. The absence of a sharp peak in curve B denotes lack of crystallinity.

Evaluation of Films

Films 0.025-0.05 cm thick were pressed at

5 230-300°C from polymer granules at 700-7000 kPa. Three of these polymers were amorphous PDD/TFE copolymers of the present invention (Polymer B is the least soluble fraction of Example 4), while the prior art crystalline copolymer was made according to the
 10 teaching of U.S. 3,978,030 to Resnick. The physical properties of these films are reported in the following Table, where it can be seen that both the modulus and the tensile strength of the amorphous copolymers of this invention are significantly improved over
 15 those of the crystalline copolymer. The amorphous copolymers are thus stiffer and stronger.

TABLE

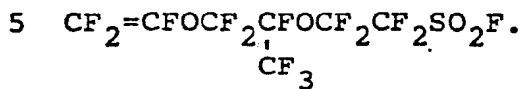
Physical Properties of TFE/PDD Copolymers

	Crystalline Copolymer	Amorphous Copolymer		
		<u>A</u>	<u>B</u>	<u>C</u>
20	<u>Mole % PDD</u>	5-7	22.1	36.6
	Tg (°C)	-	73	90
	m.p. (°C)	265	-	-
25	<u>Tensile Properties*</u> (23°C, 50% RH)			
	Modulus (MPa)	620	917	1117
	Stress (MPa)			
	Yield	15.9	26.2	-
	Maximum	20.7	27.6	27.6
30	Break	20.7	26.9	27.6
	Strain (%)			
	Yield	5.5	3.8	-
	Break	125.3	58.2	4.1
				4.4

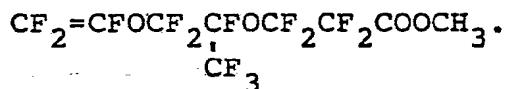
I claim:

1. An amorphous copolymer of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene, which copolymer may also contain 5 at least one other ethylenically unsaturated monomer.
2. A copolymer of Claim 1 which is a dipolymer of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene.
3. A copolymer of Claim 2 wherein the 10 proportion of perfluoro-2,2-dimethyl-1,3-dioxole is at least about 11 mole percent.
4. A copolymer of Claim 1 which also contains another ethylenically unsaturated monomer, the proportion of perfluro-2,2-dimethyl-1,3-dioxole 15 being at least 12 mole percent of the tetrafluoroethylene content, and the mole percent content of the third monomer being the smallest of all three monomers.
5. A copolymer of Claim 4 which is a 20 terpolymer of perfluoro-2,2-dimethyl-1,3-dioxole with tetrafluoroethylene and with an olefin.
6. A terpolymer of Claim 5 wherein the olefin is propylene.
7. A terpolymer of Claim 5 wherein the 25 olefin is isobutylene.
8. A terpolymer of Claim 5 wherein the olefin is ethylene.
9. A copolymer of Claim 1 which is a terpolymer of perfluoro-2,2-dimethyl-1,3-dioxole with 30 tetrafluoroethylene and another perfluoromonomer.

10. A terpolymer of Claim 9 wherein the other perfluoromonomer is 2-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoroethanesulfonyl fluoride



11. A terpolymer of Claim 9 wherein the other perfluoromonomer is methyl 3-[1-[difluoro[(trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-2,2,3,3-tetrafluoropropanoate



12. A terpolymer of Claim 9 wherein the other perfluoromonomer is perfluoropropene, perfluoro-(1,3-dioxole), or a perfluorovinyl ether.

13. A self-supporting film of an amorphous copolymer of Claim 1.

14. A self-supporting film of an amorphous copolymer of Claim 3.

25

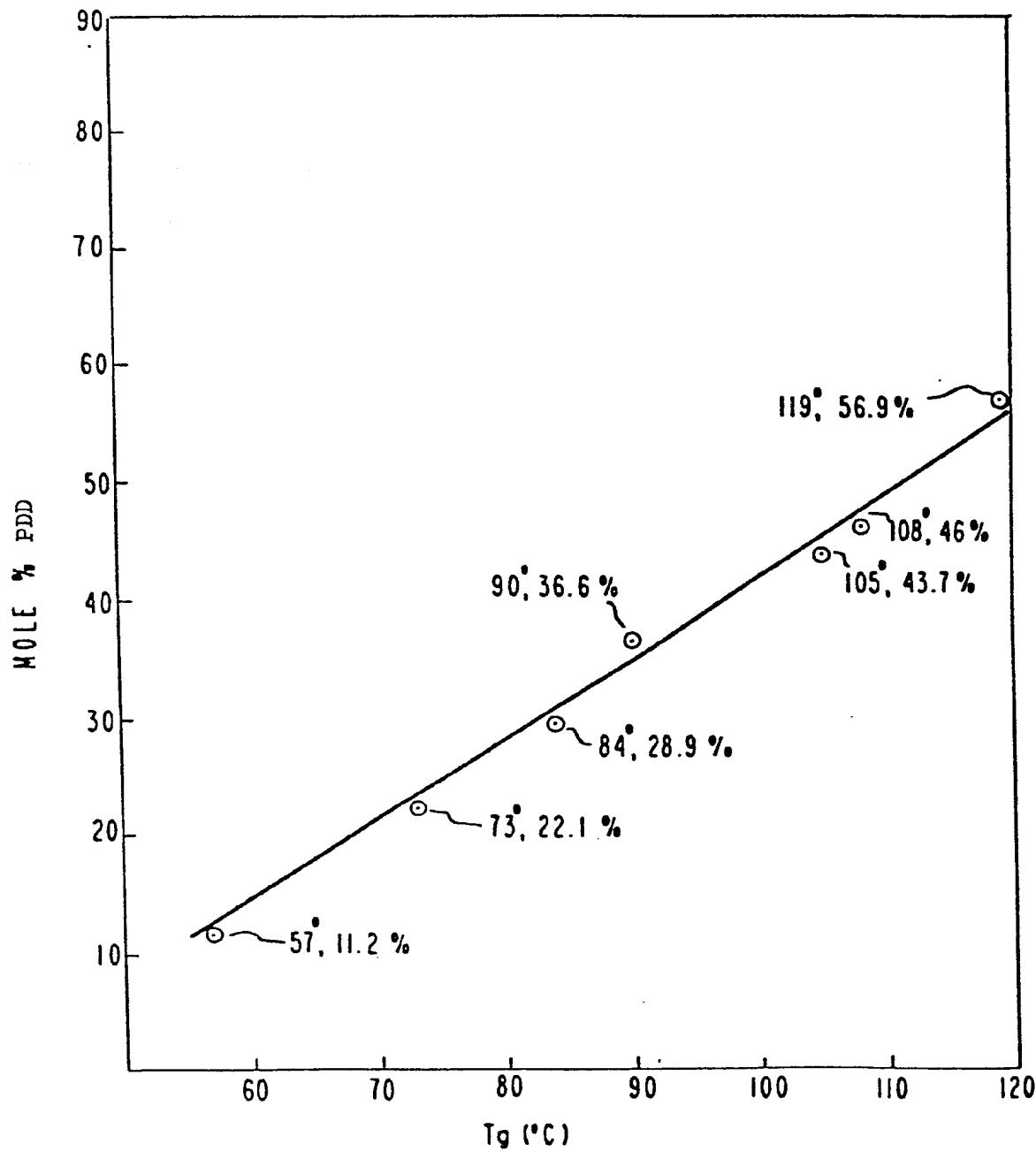
30

35

0073087

1 / 2

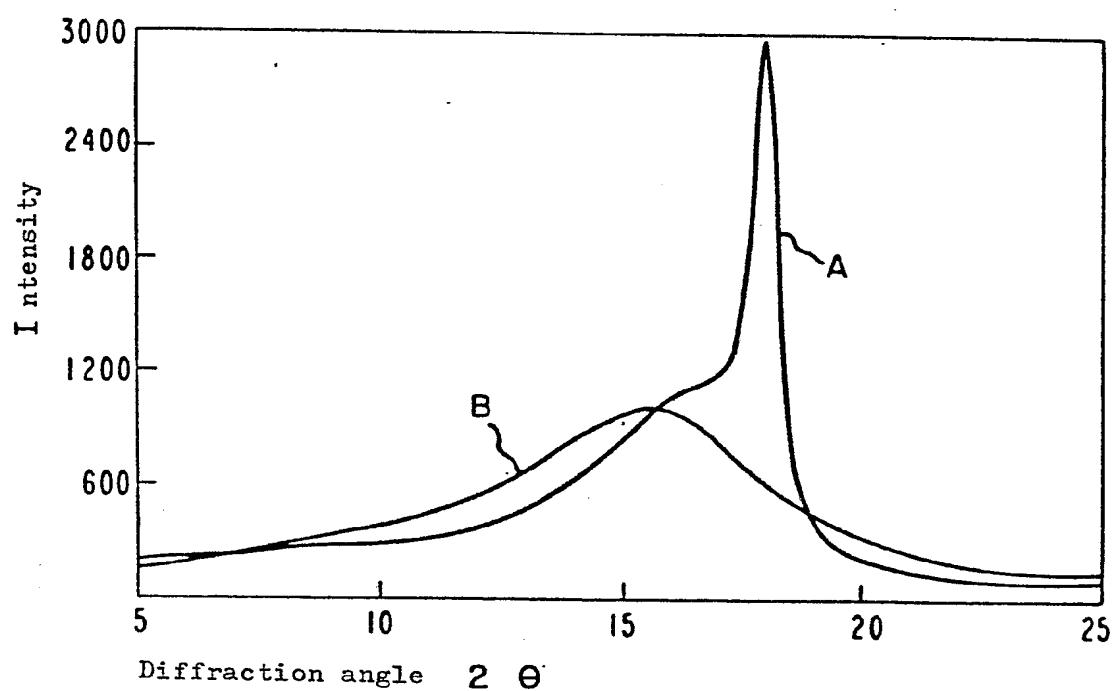
F ■ G ■ 1



0073087

2 / 2

FIG. 2





European Patent
Office

EUROPEAN SEARCH REPORT

0073087

Application number

EP 82 20 1044

DOCUMENTS CONSIDERED TO BE RELEVANT			Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages			
D, X	--- US-A-3 978 030 (P.R. RESNICK) *Claims 1,4,5; column 2, lines 14-15*		1-14	C 08 F 234/02 // (C 08 F 234/02 C 08 F 214/26 C 08 F 210/00 C 08 F 214/18
X	--- DE-A-2 227 538 (DU PONT) *Claims 1,2,5* -----		1-14	
TECHNICAL FIELDS SEARCHED (Int. Cl. 3)				
C 08 F				
The present search report has been drawn up for all claims				
Place of search THE HAGUE	Date of completion of the search 19-11-1982	Examiner CAUWENBERG C. L. M.		
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document		
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document				